Chlorine Dioxide

DOC316.53.01447

DPD Method[1] **Method 10126**

0.05 to 5.00 mg/L ClO_2 **Powder Pillows or AccuVac® Ampuls**

Scope and application: For water and wastewater. USEPA accepted for reporting for drinking water analysis.[2] This product has not been evaluated to test for chlorine and chloramines in medical applications in the United States.

[1] Adapted from Standard Methods for the Examination of Water and Wastewater.
[2] Procedure is equivalent to Standard Methods, 18 ed., 4500 ClO_2 D.

Test preparation

Before starting

Analyze the samples immediately. The samples cannot be preserved for later analysis.
Always do tests in sample cells or AccuVac© Ampuls. Do not put the instrument in the sample or pour the sample into the cell holder.
Make sure that the sample cells are clean and there are no scratches where the light passes through them.
Rinse the sample cell and cap with the sample three times before the sample cell is filled.
Make sure that there are no fingerprints or liquid on the external surface of the sample cells or AccuVac© Ampuls. Wipe with a lint-free cloth before measurement.
Cold waters can cause condensation on the sample cell or bubbles in the sample cell during color development. Examine the sample cell for condensation or bubbles. Remove condensation with a lint-free cloth. Invert the sample cell to remove bubbles.
Install the instrument cap over the cell holder before ZERO or READ is pushed.
After the test, immediately empty and rinse the sample cell. Rinse the sample cell and cap three times with deionized water.
If the chlorine dioxide concentration in the sample exceeds the upper limit of the test, the color may fade or the sample color may change to yellow. Dilute the sample with a known volume of high quality, chlorine demand-free water and repeat the test. Some loss of chlorine dioxide may occur due to the dilution. Multiply the result by the dilution factor.
Do not use the same sample cells for free and total chlorine. If trace iodide from the total chlorine reagent is carried over into the free chlorine determination, monochloramine will interfere. It is best to use separate, dedicated sample cells for free and total chlorine measurements.
The AccuVac Ampul Snapper makes AccuVac Ampul tests easier to do. The AccuVac Ampul Snapper keeps the broken tip of the ampul, prevents exposure to the sample and provides controlled conditions for filling the ampule.
An AccuVac Ampul for Blanks can be used to zero the instrument in the AccuVac test procedure.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.

Items to collect

Powder pillows

Description	Quantity
DPD Free Chlorine Reagent Powder Pillow, 10-mL	1
Glycine Reagent	4 drops
Sample cells, 25-mm (10 mL)	2

Refer to Consumables and replacement items on page 7 for order information.

AccuVac Ampuls

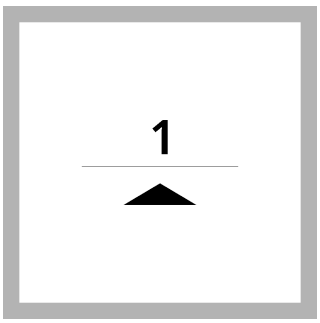
Description	Quantity
DPD Free Chlorine Reagent AccuVac® Ampul	1
Glycine Reagent	16 drops
Beaker, 50-mL	1
Stopper for 18-mm tubes and AccuVac Ampuls	1
Sample cell, 25-mm (10 mL)	1

Refer to Consumables and replacement items on page 7 for order information.

Sample collection

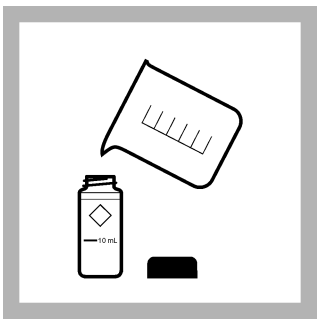
- Analyze the samples immediately. The samples cannot be preserved for later analysis.
- Chlorine dioxide is a strong oxidizing agent and is unstable in natural waters. Chlorine reacts quickly with various inorganic compounds and more slowly with organic compounds. Many factors, including reactant concentrations, sunlight, pH, temperature and salinity influence the decomposition of chlorine dioxide in water.
- Collect samples in clean glass bottles. Do not use plastic containers because these can have a large chlorine dioxide demand.
- Pretreat glass sample containers to remove chlorine dioxide demand. Soak the containers in a weak bleach solution (1 mL commercial bleach to 1 liter of deionized water) for at least 1 hour. Rinse fully with deionized or distilled water. If sample containers are rinsed fully with deionized or distilled water after use, only occasional pretreatment is necessary.
- Make sure to get a representative sample. If the sample is taken from a spigot or faucet, let the water flow for at least 5 minutes. Let the container overflow with the sample several times and then put the cap on the sample container so that there is no headspace (air) above the sample.

Powder pillow procedure

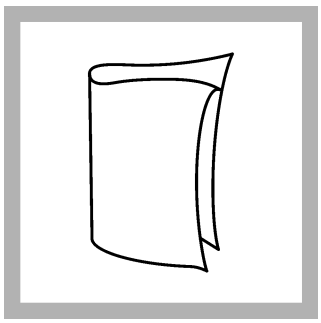


1. Set the instrument to channel 1.

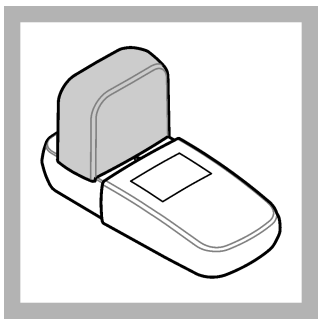
For DR300, push the up arrow button. For PCII, push the menu button, checkmark button, then the menu button again.



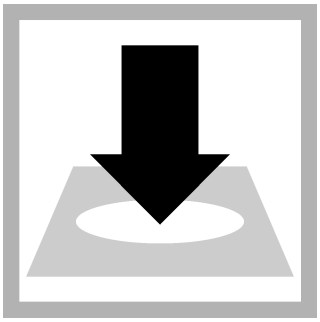
2. Prepare the blank: Rinse a sample cell and cap three times with sample. Fill the sample cell to the 10-mL mark with sample. Close the sample cell.



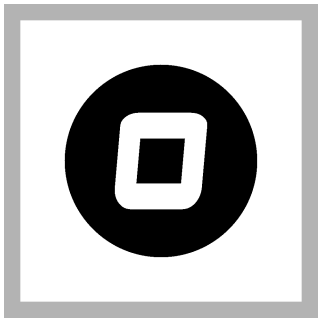
3. Clean the blank sample cell.



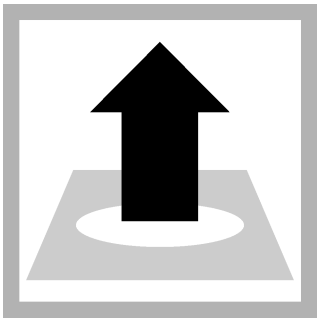
4. Install the instrument cap over the cell holder.



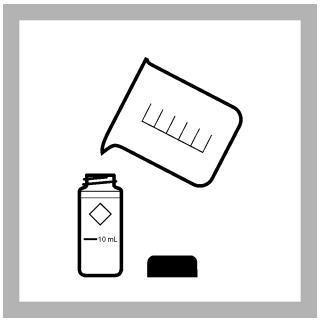
5. Insert the blank into the cell holder. Point the diamond mark on the sample cell toward the keypad.



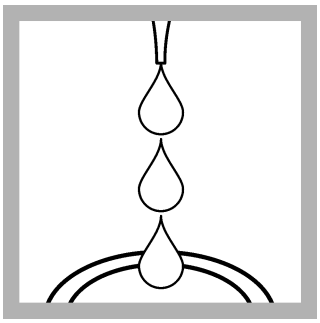
6. Push **ZERO**. The display shows “0.00”.



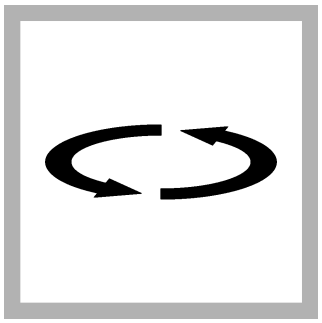
7. Remove the sample cell from the cell holder.



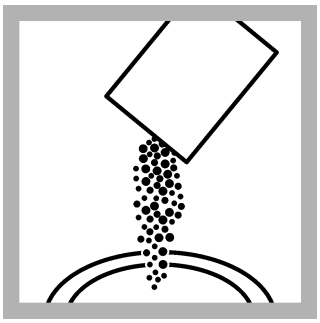
8. Prepare the sample: Fill a second sample cell to the 10-mL mark with sample. Complete steps 9–12 quickly.



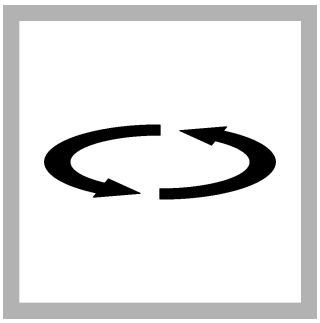
9. Add 4 drops of Glycine Reagent to the sample cell.



10. Swirl to mix.

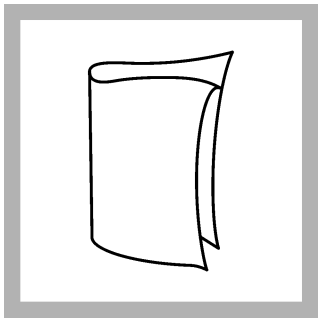


11. Add the contents of one DPD Free Chlorine Powder Pillow to the sample cell.

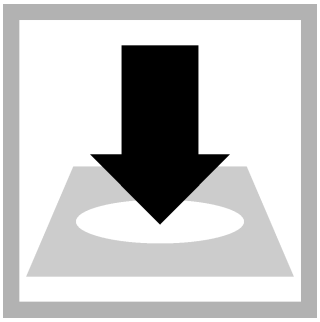


12. Swirl the sample cell for 20 seconds to mix.
Do not shake or invert the sample cell. A pink color will show if ClO_2 is in the sample.

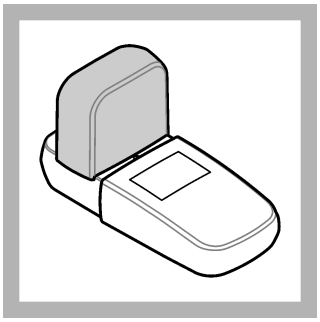
13. Wait 30 seconds for any undissolved powder to settle. Undissolved powder will not affect accuracy.



14. Clean the prepared sample cell.



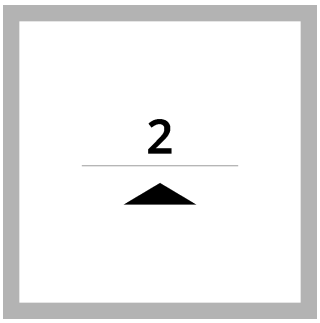
15. Within 1 minute of the reagent addition, insert the prepared sample into the cell holder. Point the diamond mark on the sample cell toward the keypad.



16. Install the instrument cap over the cell holder.

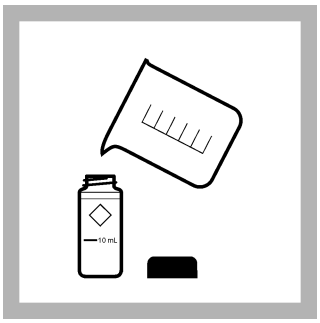
17. Push **READ**. Results show in mg/L chlorine dioxide (ClO_2).

AccuVac® Ampul procedure

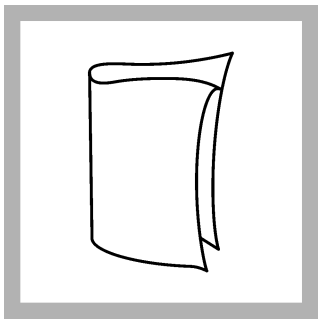


1. Set the instrument to channel 2.

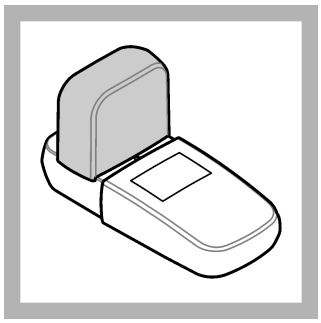
For DR300, push the up arrow button. For PCII, push the menu button, checkmark button, then the menu button again.



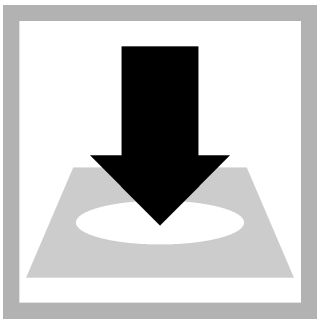
2. Prepare the blank: Rinse a sample cell and cap three times with sample. Fill the sample cell to the 10-mL mark with sample. Close the sample cell.



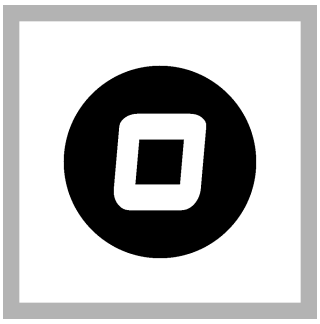
3. Clean the blank sample cell.



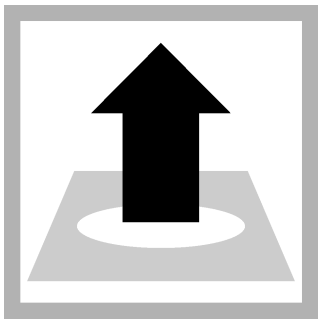
4. Install the instrument cap over the cell holder.



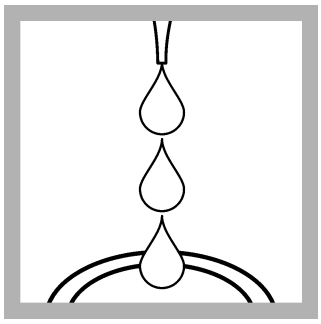
5. Insert the blank into the cell holder. Point the diamond mark on the sample cell toward the keypad.



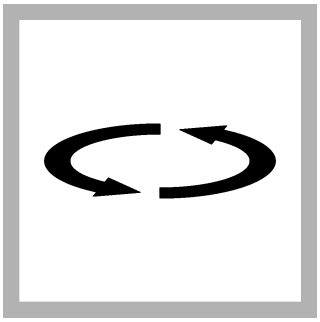
6. Push **ZERO**. The display shows “0.00”.



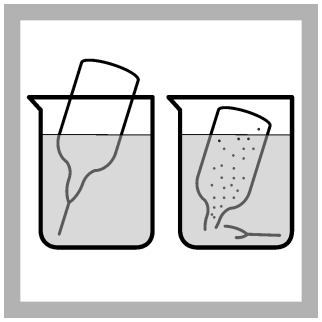
7. Remove the sample cell from the cell holder.



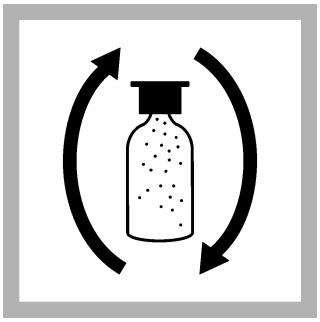
8. Prepare the sample: Collect at least 40 mL of sample in a 50-mL beaker. Add 16 drops of Glycine Reagent to the sample in the beaker. Do steps 9–12 quickly and without too much agitation.



9. Swirl to mix.

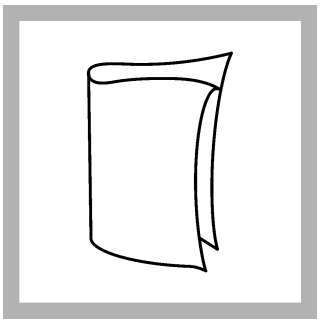


10. Fill the AccuVac Ampul with the prepared sample. Keep the tip immersed while the Ampul fills completely. Close the Ampul.

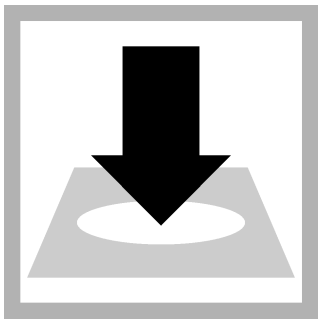


11. Quickly invert the AccuVac Ampul several times to mix.

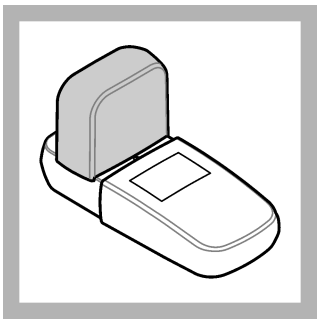
12. Wait 30 seconds for any undissolved powder to settle. Undissolved powder will not affect accuracy.



13. Clean the AccuVac Ampul.



14. Within 1 minute of the reagent addition, insert the prepared sample AccuVac Ampul into the cell holder.



15. Install the instrument cap over the cell holder.

16. Push **READ**. Results show in mg/L chlorine dioxide (ClO_2).

Interferences

Interfering substance	Interference level
Acidity	More than 150 mg/L $CaCO_3$. The full color may not develop or the color may fade instantly. Adjust to pH 6–7 with 1 N Sodium Hydroxide. Measure the amount to add on a separate sample aliquot, then add the same amount to the sample that is tested. Correct the test result for the dilution from the volume addition.
Alkalinity	More than 250 mg/L $CaCO_3$. The full color may not develop or the color may fade instantly. Adjust to pH 6–7 with 1 N Sulfuric Acid. Measure the amount to add on a separate sample aliquot, then add the same amount to the sample that is tested. Correct the test result for the dilution from the volume addition.
Bromine, Br_2	Positive interference at all levels
Chlorine Dioxide, ClO_2	Positive interference at all levels
Chloramines, organic	May interfere
Hardness	No effect at less than 1000 mg/L as $CaCO_3$
Manganese, Oxidized (Mn^{4+}, Mn^{7+}) or Chromium, Oxidized (Cr^{6+})	Pre-treat the sample as follows: **1.** Adjust the sample pH to 6–7. **2.** Add 3 drops of Potassium Iodide (30-g/L) to 10 mL of sample. **3.** Mix and wait 1 minute. **4.** Add 3 drops of Sodium Arsenite (5-g/L) and mix. **5.** Use the test procedure to measure the concentration of the treated sample. **6.** Subtract this result from the result without the treatment to obtain the correct chlorine concentration.

Interfering substance	Interference level
Ozone	Positive interference at all levels
Peroxides	May interfere
Highly buffered samples or extreme sample pH	Can prevent the correct pH adjustment (of the sample) by the reagents. Sample pretreatment may be necessary. Adjust to pH 6–7 with acid (Sulfuric Acid, 1 N) or base (Sodium Hydroxide, 1 N). Correct the test result for the dilution caused by the volume additions.

Pollution prevention and waste management

If sodium arsenite was added to the sample for manganese or chromium interferences, the reacted samples will contain arsenic and must be disposed of as a hazardous waste. Dispose of reacted solutions according to local, state and federal regulations.

Accuracy check

Standard solution method

Use the standard solution method to validate the test procedure, the reagents and the instrument.

The manufacturer does not recommend preparation of chlorine dioxide standards. These standards are explosive and volatile! Only a trained chemist should prepare the standards with appropriate safety equipment and precautions. If independent standard preparation is required, refer to the instructions in *Standard Methods for the Examination of Water and Wastewater*, Part 4500-ClO2 Chlorine Dioxide, under the headings "Stock chlorine dioxide solution" and "Standard chlorine dioxide solution".

Because the preparation of chlorine dioxide is difficult and hazardous, chlorine standards are used for calibration and to validate the chlorine dioxide test procedure, the reagents and the instrument.

Items to collect:

- Chlorine Standard Solution Voluette™ Ampules, 50–75 mg/L, 10-mL (use mg/L on label)
- Ampule breaker
- Pipet, TenSette®, 0.1–1.0 mL and tips
- Volumetric flask, 100-mL
- Chlorine demand-free deionized water

1. Prepare a 1-mg/L free chlorine standard:
   a. Determine the concentration of the standard from the certificate of analysis supplied with the standard (50–75 mg/L Cl_2). Calculate the volume of standard needed as follows:

      100 ÷ standard concentration = mL standard necessary
   b. Use the TenSette pipet to add the volume of standard necessary into a 100-mL volumetric flask.
   c. Dilute to the mark with chlorine demand-free deionized water. Invert to mix.
2. Use the test procedure to measure the concentration of the prepared standard. Do not add the Glycine Reagent drops.
3. If the test result is 2.4 times higher than the chlorine concentration, the DPD Free Chlorine Reagent operation and the instrument operation are correct.
4. Use the test procedure again to measure the concentration of the prepared standard. Add the Glycine Reagent drops this time.
5. If the test result is less than 0.10 mg/L ClO_2, the Glycine Reagent removed the free chlorine interference.

A verification of the internal, factory set calibration may be a requirement of a regulatory official or primacy agency. Use a 1-mg/L free chlorine check standard to verify or adjust the calibration curve using the Standard Calibration Adjust feature.

Method performance

The method performance data that follows was derived from laboratory tests that were measured on a DR300 and a Pocket Colorimeter II during ideal test conditions. Users can get different results under different test conditions.

Precision (95% confidence interval)
4.78 ± 0.22 mg/L ClO_2 (AccuVac Ampules), 2.08 ± 0.04 mg/L ClO_2 (Powder Pillows)

Summary of method

Chlorine dioxide reacts with DPD (N, N-diethyl-p-phenylenediamine) to the extent of one-fifth of its total available chlorine content, which corresponds to the reduction of chlorine dioxide to chlorite. A pink color forms, the intensity of which is proportional to the chlorine dioxide concentration in the sample. Chlorine interference is removed with the addition of glycine, which converts free chlorine to chloroaminoacetic acid, but has no effect on chlorine dioxide at the test pH.

Consumables and replacement items

Required reagents

Description	Quantity/test	Unit	Item no.
Chlorine Dioxide DPD/Glycine Reagent Set	1	100/pkg	2770900
Includes:			
DPD Free Chlorine Reagent Powder Pillow, 10 mL	1	100/pkg	2105569
Glycine Reagent	4 drops	29 mL	2762133
OR			
Chlorine Dioxide DPD/Glycine AccuVac® Ampul Reagent Set	1	25/pkg	2771000
Includes:			
DPD Free Chlorine Reagent AccuVac® Ampul	1	25/pkg	2502025
Glycine Reagent	16 drops	29 mL	2762133

Required apparatus (powder pillows)

Description	Quantity/test	Unit	Item no.
Sample cells, 10-mL round, 25 mm x 60 mm	2	6/pkg	2427606

Required apparatus (AccuVac Ampul)

Description	Quantity/Test	Unit	Item no.
Sample cell, 10-mL round, 25 mm x 60 mm	1	6/pkg	2427606
Beaker, 50 mL	1	each	50041H
Stoppers for 18-mm tubes and AccuVac Ampuls	2	6/pkg	173106

Optional reagents and apparatus

Description	Unit	Item no.
Chlorine Standard Solution, 2-mL PourRite® Ampules, 50–75 mg/L	20/pkg	1426820
Chlorine Standard Solution, 10-mL Voluette® Ampule, 50–75 mg/L	16/pkg	1426810
Ampule Breaker, 10-mL Voluette® Ampules	each	2196800
PourRite® Ampule Breaker, 2-mL	each	2484600

Optional reagents and apparatus (continued)

Description	Unit	Item no.
Flask, volumetric, Class A, 100 mL, glass, Certified	each	2636642
Flask, volumetric, Class A, 100 mL, glass	each	1457442

Optional reagents and apparatus

Description	Unit	Item no.
AccuVac® Ampul Snapper	each	2405200
AccuVac® Ampul vials for sample blanks	25/pkg	2677925
DPD Free Chlorine Reagent Powder Pillows, 10 mL	1000/pkg	2105528
DPD Free Chlorine Reagent Powder Pillows, 10 mL	300/pkg	2105503
Potassium Iodide, 30-g/L	100 mL	34332
Sodium Arsenite, 5-g/L	100 mL	104732
Sodium Hydroxide Standard Solution, 1.0 N	100 mL MDB	104532
Standard Methods for the Examination of Water and Wastewater (current edition)	each	2270800
Stoppers for 18-mm tube	25/pkg	173125
Sulfuric Acid Standard Solution, 1 N	100 mL MDB	127032
Pipet, TenSette®, 0.1–1.0 mL	each	1970001
Pipet tips for TenSette® Pipet, 0.1–1.0 mL	50/pkg	2185696
Pipet tips for TenSette® Pipet, 0.1–1.0 mL	1000/pkg	2185628
Paper, pH, 0–14 pH range	100/pkg	2601300

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